Journal of Applied Electrochemistry **30**: 1169–1172, 2000.

An interpretation of the Zech–Podlaha–Landolt model of metal codeposition via queuing theory

T.Z. FAHIDY
Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Received 13 December 1999; accepted in revised form 23 May 2000

Key words: deposition, electrolysis, iron, nickel, queuing theory

Abstract

The electrode kinetics of anomalous codeposition of iron group metals is interpreted by queuing theory applied to the recently proposed Zech–Podlaha–Landolt model which postulates an adsorbed mixed–metal species existing temporarily as an electrochemically activated complex. The complex acts as an intermediate in a consecutive reaction leading to enhanced deposition of the more electronegative metal. Numerical illustrations for the codeposition of iron and nickel, and cobalt and nickel from a sulphate electrolyte are provided.

List of symbols

b	Tafel parameter (V^{-1})
c_i	concentration of species i (mol cm^{-3})
E	electrode potential (V)
$I_q(z)$	modified Bessel function of the first kind of order q, argument z
L	expected number of individuals in the system
L_q	expected number of individuals in the line
N	upper limit of the number of individuals
N_A	Avogadro's number (6.028×10^{23} ion mol^{-1})
N_i	ion flux of species i (ion cm^{-2} s^{-1})
n	number of individuals
k_1^0	specific electrode reaction rate constant (Equation 1; cm^4 mol^{-1} s^{-1})
k_2^0	specific electrode reaction rate constant (Equation 2; mol cm^{-2} s^{-1})
$P_n(t)$	probability of n individuals present at time t
p_n	equilibrium probability of n individuals present
V	variance of the number of individuals present
W_q	mean waiting time in the line (fs or as)

Greek symbols

θ_1	surface coverage of adsorbed metal species 1
θ_2	surface coverage of adsorbed metal species 2
θ_z	surface coverage of an adsorbed mixed – metal species
λ	arrival rate (fs^{-1} or as^{-1})
μ	service rate (fs^{-1} or as^{-1})
ρ	traffic density

Acronyms

EAC	electrochemically activated complex (Equations 1 and 2)
MSE	mercury sulphate electrode
SHE	standard hydrogen electrode

1. Introduction

The anomalous codeposition of iron group metals, and especially the inhibition of Ni deposition in the presence of Fe, has been the subject of analysis since the sixties; various mechanisms involving surface adsorption as well as electrode processes have recently been discussed by Pritzker [1, 2] and Zech et al. [3, 4]. The model presented by the latter is a modification of two parallel single metal depositions in two consecutive steps proposed by Matlosz [5]. The Zech–Podlaha–Landolt model assumes the temporary formation of a mixed-metal adsorbate on the electrode surface followed by its decomposition according to the scheme:

$$M_1(II) + M_2(II) + e^- \rightarrow [M_1M_2(III)]_{ads} \quad (1)$$

$$[M_1M_2(III)]_{ads} + e^- \rightarrow M_1(II) + M_2(s) \quad (2)$$

In these steps a preferential deposition of metal M_2 is postulated in addition to single ion deposition paths formulated by Matlosz. Numerical simulations performed by Zech et al. [4] compare at least semi-quantitatively with experimental determinations [3] of metal deposition parameters. However, model predictions are strongly linked to the numerical values of deposition parameters, hence "practical application for the quantitative prediction of alloy composition is limited due to uncertainties in the prevailing electrode

reaction mechanisms'' [4]. These caveats notwithstanding, the supposition of a mixed-metal adsorbate intermediate widens the horizon of the anomalous codeposition problem in terms of the electrochemically activated complex (EAC) inherent in the new kinetic model.

The purpose of this paper is to characterize the path of the EAC via queuing theory, whose application to certain anodic dissolution phenomena has recently been demonstrated [6, 7]. In this framework, arrival is the queuing-theory equivalent of the electrode process in Equation 1, and service is the equivalent of the electrode process in Equation 2. The specific rates k_1 and k_2 (k_{31} and k_{32} in [4]) are employed in the computation of arrival and service rates, respectively, which are the fundamental parameters of a queuing process. Using its conventional terminology, the 'system' is defined as the overall process involving the formation and decomposition of the EAC, and the 'line' is defined as the species at the electrode surface ready to form the EAC. Queuing theory is used to predict the expected number in the system, its variance, the expected number in the line, the average waiting time in the line, and various probabilities related to the existence of species in the system at a given time, or at steady state. The compatibility of queuing theory concepts with electrode processes was indicated in an earlier seminal work in electrochemistry [8].

Queuing processes of the kind can be classified into the immigration – emigration class category of linear birth – death processes [9]. If the probability distribution of arrival ('birth') and service ('death') are known, the rates are determined by statistical parameters of these distributions. In the sequel, the arrival distribution is considered to be poissonian, that is, that EAC formation is independent, within a certain time interval, of the interval itself. The service time distribution is considered to be exponential. Justification for the poissonian arrival/exponential service time model is provided in a previous paper [6], emphasizing cross-fertilization of different principles.

2. Summary of pertinent queuing theory

The concepts and nomenclature follow closely Sections 2.5a, 2.5b and 4.2 of Saaty [10]. Let $P_n(t)$ be the probability that there are n individuals (or items) in the system at time instant t, given that there were i individuals (or items) in it at zero time ($t = 0$ is the starting instant of the queuing process). The temporal variation of this probability is given by the differential equation set

$$\frac{dP_n}{dt} = -(\lambda+\mu)P_n(t) + \lambda P_{n-1}(t) + \mu P_{n+1}(t) \quad \text{where } n \geq 1 \tag{3}$$

$$\frac{dP_0}{dt} = -\lambda P_0(t) + \mu P_1(t) \tag{4}$$

where λ and μ are the constant rates of arrival and service, respectively. The ratio $\rho = \lambda/\mu$ is called the traffic density. If the ratio is unity, there is no queue, since arrival and service are exactly matched. If the ratio is larger than unity, the queue is infinite. The solution of Equations 3 and 4 are

$$P_n(t) = \exp[-(\lambda+\mu)t]\left[(\mu/\lambda)^{(i-n)/2} I_{n-i}(2t\sqrt{\lambda\mu}) + (\mu/\lambda)^{(i-n+1)/2} I_{n+1+i}(2t\sqrt{\lambda\mu}) + (1-\rho)(\rho^n)\sum_{k=n+i+2}^{\infty}(\mu/\lambda)^{k/2} I_k(2t\sqrt{\lambda\mu})\right] \tag{5}$$

in terms of modified Bessel functions of the first kind.

The related expression

$$\sum_{n=j}^{\infty} P_n(t) = [\exp -(\lambda+\mu)t]\left[\sum_{n=j-i}^{\infty}\rho^{n/2}\cdot I_n(2t\sqrt{\lambda\mu}) + \sum_{n=j+1+i}^{\infty}(\mu/\lambda)^{(n-2j)/2} I_n(2t\sqrt{\lambda\mu})\right] \tag{6}$$

yields the probability that the number of individuals (or items) in the system is not less than j at a given time instant t, if there were i individuals (or items) in it at zero time. If the traffic density is less than unity, a steady-state queue is eventually established, and Equations 3 and 4 yield the algebraic equation set

$$(\lambda+\mu)p_n = \lambda p_{n-1} + \mu p_1 \quad \text{where } n \geq 1 \tag{7}$$

$$\lambda_{p_0} = \mu_{p_1} \tag{8}$$

where $p_n = \lim P_n(t)$ as $t \to \infty$. Recursive solution of Equations 7 and 8 yields the geometric probability distribution $p_0 = 1-\rho$ and $p_n = \rho^n(1-\rho)$. The following steady state queue characteristics are of particular interest for the subject matter of this paper.

Expected number of individuals/items in the system:

$$L \equiv \sum_{n=0}^{\infty} np_n = \rho/(1-\rho) \tag{9}$$

with variance

$$V \equiv \sum_{n=0}^{\infty}(n-L)^2 p_n = L + L^2 \tag{10}$$

Expected number of individuals/items in the line:

$$L_q \equiv \sum_{n=0}^{\infty}(n-1)p_n = \rho^2(1-\rho) \tag{11}$$

Expected length of waiting time in the line:

$$W_q \equiv L_q/\lambda \tag{12}$$

In many practical applications the summations above are terminated at a sufficiently large integer $N < \infty$, whose value is prescribed such that for all $n > N, p_N$ is vanishingly small.

3. Application to the electrolytic deposition of Fe–Ni and Co–Ni from sulphate solutions: a numerical illustration

Table 1 contains pertinent quantities for the establishment of the fundamental parameters λ and μ. The species flux was computed using Table 1 in [4], as

$$N_1 = N_A k_1^0 c_1 c_2 (1 - \theta_1 - \theta_2 - \theta_z)^2 \exp(-b_1 E) \qquad (13)$$

and

$$N_2 = N_A k_2^0 \theta_z \exp(-b_2 E) \qquad (14)$$

The time scale was chosen to match the queue to a small number of species participating in the process, that is, 1 fs $\equiv 10^{-15}$ s for the first illustrative case, and 0.1 fs for the second illustrative case.

Transient probabilities of finding stated numbers of the EAC at selected times are shown in Tables 2 and 3. The entries were conveniently computed via Equation 6 with $N = 9$ providing adequate accuracy, then by the relationships

$$P_0 \approx 1 - \sum_{n=1}^{9} P_n \qquad (15a)$$

$$P_1 \approx \sum_{n=1}^{9} P_n - \sum_{n=2}^{9} P_n \qquad (15b)$$

$$P_2 \approx \sum_{n=2}^{9} P_n - \sum_{n=3}^{9} P_n \qquad (15c)$$

Table 1. Numerical values of parameters in the Fe–Ni and the Co–Ni deposition process selected for illustration

Parameter and unit	Illustration 1 (Fe–Ni)	Illustration 2 (Co–Ni)
*E(NSE)/V	−1.4	−1.35
‡E(SHE)/V	−0.784	−0.734
†$(\theta_1 + \theta_2)$	0.0029	0.40
*θ_z	0.96	0.58
†$c_1 c_2$/(mol cm^{-3})^2	4×10^{-9}	5×10^{-9}
*k_1^0/cm^4 mol^{-1} s^{-1}	4×10^{-4}	4×10^{-5}
*k_2^0/mol cm^{-2} s^{-1}	4×10^{-15}	4×10^{-14}
*b_1, b_2/V^{-1}	19	19
‡N_1/ion cm^{-2} s^{-1}	3.906×10^{15}	1.005×10^{16}
‡N_2/ion cm^{-2} s^{-1}	6.814×10^{15}	1.599×10^{16}
‡τ, time frame for the queuing process/fs	1	0.1
‡$\lambda\ \tau^{-1}$	3.906	1.005
‡$\mu\ \tau^{-1}$	6.814	1.599
‡ρ	0.573	0.628

*data in [4]
†assumed
‡computed from data in [4]

Table 2. Transient probabilities of finding X number of EAC in the queue at selected times, with parameters in Illustration 1* (Fe–Ni)

Time/fs	$X = 0$; $P_0(t)$	$X = 1$; $P_1(t)$	$X = 2$; $P_2(t)$	Pr [$X > 2$]
0	1	0	0	0
0.1	0.758	0.204	0.0338	0.0042
0.3	0.595	0.271	0.0979	0.0361
0.5	0.533	0.268	0.168	0.0310
0.7	0.501	0.262	0.133	0.104
1.0	0.485	0.257	0.136	0.122
∞†	0.427	0.245	0.140	0.188

*assuming no species at zero time (i.e. immediately prior to the onset of the deposition) process
†computed as $p_n = \rho^n(1 - \rho)$; $\rho = 0.573$

Table 3. Transient probabilities of finding X number of EAC in the queue at selected times, with parameters in Illustration 2* (Co–Ni)

Time/0.1 fs	$X = 0$; $P_0(t)$	$X = 1$; $P_1(t)$	$X = 2$; $P_2(t)$	Pr [$X > 2$]
0	1	0	0	0
0.1	0.926	0.0712	2.7×10^{-3}	1.3×10^{-4}
0.3	0.779	0.191	0.0270	3.3×10^{-3}
0.5	0.718	0.176	0.0460	0.0598
0.7	0.647	0.263	0.0730	0.0173
1.0	0.589	0.278	0.0980	0.0346
∞†	0.372	0.234	0.147	0.247

*assuming no species present at zero time (i.e. immediately prior to the onset of the electrode process)
†computed as $p_n = \rho^n(1 - \rho)$; $\rho = 0.628$

The numerical values of the modified Bessel functions were obtained from conventional tabulations [11, 12].

4. Discussion

The foregoing results indicate that queuing theory predicts a time horizon of 0.1–300 as for the passage of Fe(II) and Ni(II) ions, and of 1–1000 as for the passage of Co(II) and Ni(II) ions through the intermediate adsorbate complex to the final surface state, in the two specific numerical illustrations. The time horizon is a function of surface coverage (i.e., electrode potential), electrolyte composition and concentration, and electrode kinetic (Tafel) parameters. These parameters are 'compressed' by queuing theory into the arrival and service rate, hence the traffic density. The numerical values of the latter are not appreciably different, but the arrival and service rates themselves differ noticeably from the Fe–Ni to the Co–Ni system. These differences are reflected by the numerical values of the transient probabilities (Tables 2 and 3) and the steady-state queue properties (Table 4).

One particular effect of the traffic density is demonstrated by the steady-state probability distributions. In the Co–Ni case, with a traffic density about 1.1 times higher than in the Fe–Ni case, the probability of finding no species passing through the process represented by Equation 1 decreases by about 13%, but the probability of one or two transitions is not affected noticeably

Table 4. Steady state properties in the queues of the numerical illustrations

Property	Illustration 1; $\rho = 0.573$	Illustration 2; $\rho = 0.628$
L^*	1.342	1.689
V	1.830	2.339
L_q †	0.768	1.059
W_q ‡	0.197 (fs)	1.054 (as)

* interpreted as the expected number of $M_1(II)$, $M_2(II)$ and EAC species

† interpreted as the expected number of the $M_1(II)$ and $M_2(II)$ species

‡ interpreted as the mean reaction time required for the formation of the EAC

(about 4% when $X = 1$, and about 5% when $X = 2$). The finding that Pr $[X \geqslant 2]$ is about 20% larger in the Co–Ni case is probably due to the higher service rate associated with the Fe–Ni system, ensuring a somewhat more efficient 'no congestion' conditions for passage through the intermediate adsorbate complex state.

Some comments are in order with respect to the assumption of an exponential service time (i.e., EAC decomposition time) distribution. As discussed in [6], this assumption is equivalent to the assumption that the electrode surface behaves as a Markovian process generator [13]. Given the importance of Markov processes in the modern interpretation of natural phenomena (e.g., [14–16]), this is a plausible assumption, especially in view of our limited understanding of the anomalous nature of iron alloy deposition. Were the *experimental* distribution of EAC lifetime known, the variance of the distribution could be used via the important Pollaczek–Khintchine theorem [7, 10] to estimate the expected number of species in the queue, and the mean value of waiting time in it. In other words, no postulate of a (theoretical) service time distribution would be needed.

5. Final remarks

The queuing theory model employed in this paper considers the electrode surface as a 'single queue server', and does not discriminate between individual active centres on the surface. Thus, it is immaterial in this context, whether a single queue, or a large number of identical parallel queues are postulated. Tenets of queuing theory, capable of dealing with parallel queues of different traffic densities etc., would not be of much use, unless the distribution of surface activity along an electrode are known. This aspect is well beyond the scope of the current subject matter.

Acknowledgement

This research has been supported by the Natural Sciences and Engineering Research Council of Canada (NSERC).

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